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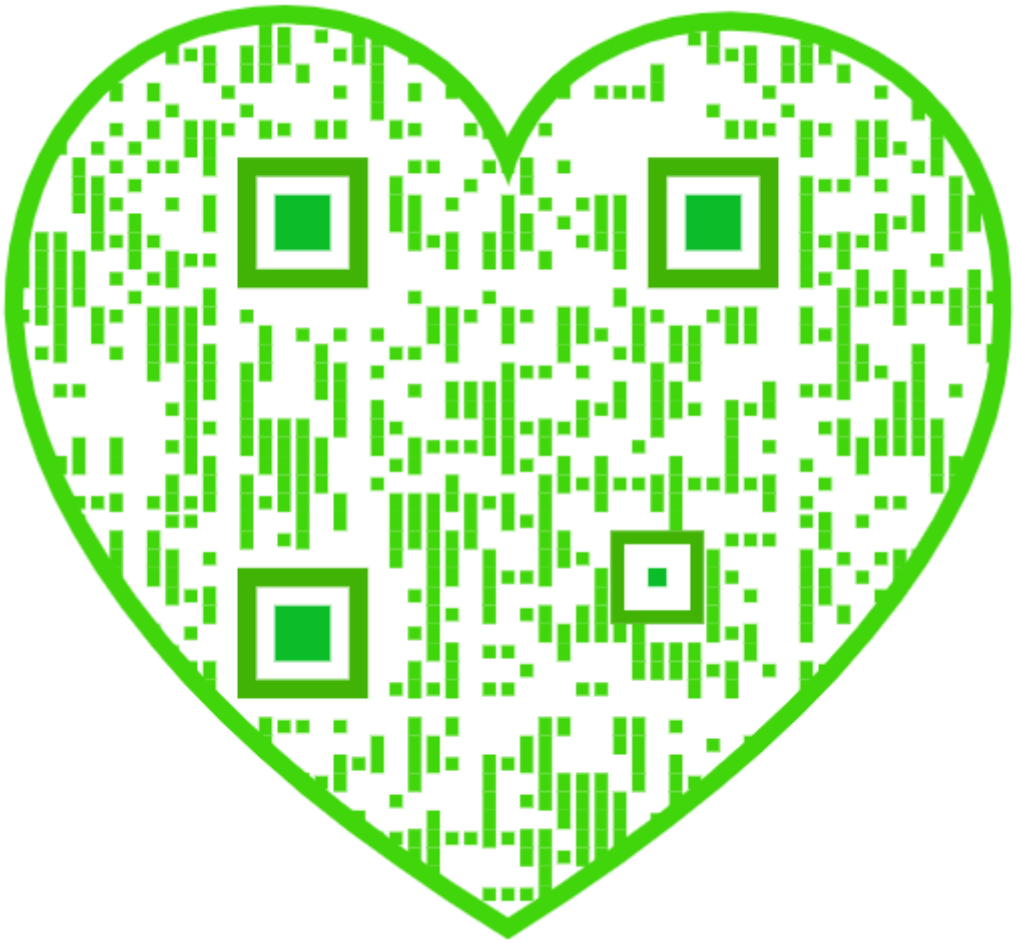

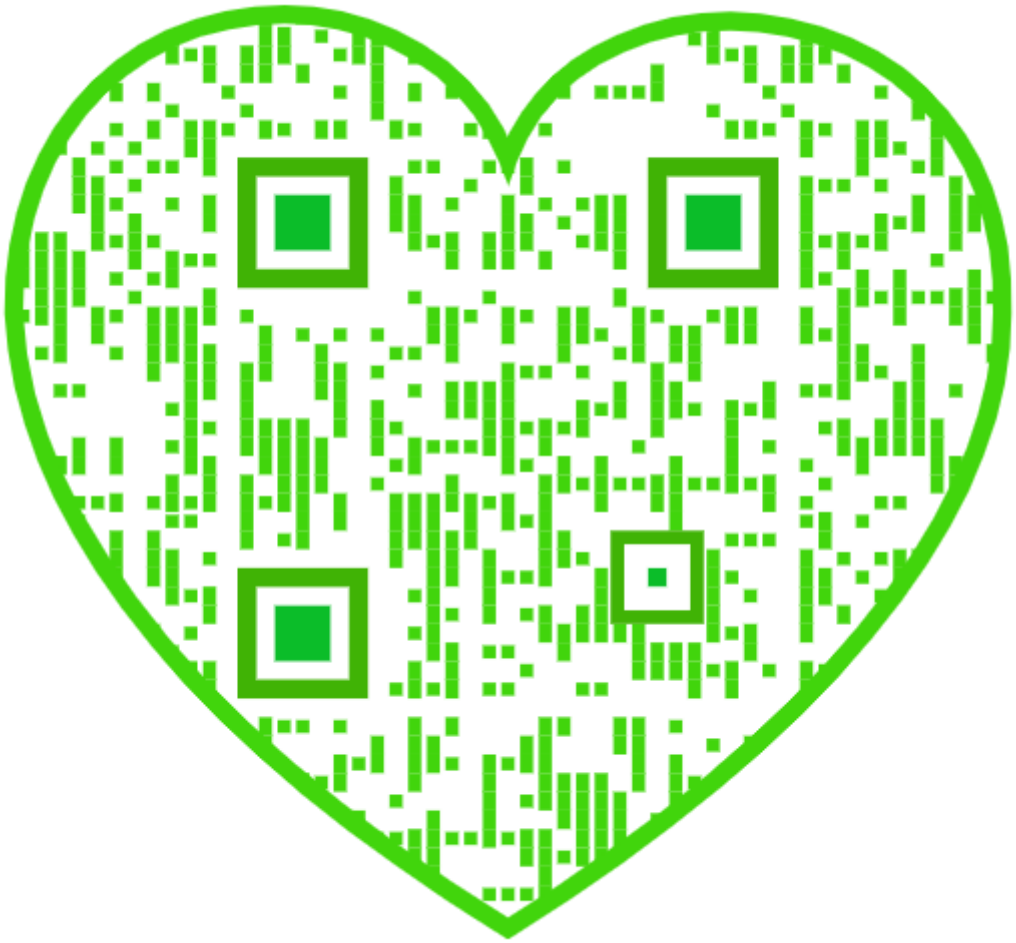

# LABORATORY NOTES.

## SANITARY CHEMISTRY

AND

## WATER ANALYSIS.

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# LABORATORY NOTES ON SANITARY CHEMISTRY.

[Prepared for the use of students in the Laboratory of Sanitary Chemistry of the Massachusetts Institute of Technology. Not published.]

THE application of chemistry to problems of public health or general sanitation is of comparatively recent date, and its importance can hardly be overrated from the present standpoint of the relation between health and the condition of air, water, and food materials as regards the action of the lower forms of life. Soil and food are the hotbeds in which these lower forms of life are propagated and from which they are carried by water and air as well as by actual contact. Sanitary biology is concerned with the organisms themselves; sanitary chemistry with the detection and interpretation of the changes which they cause in the materials in which they grow, and with the production of certain substances inimical to health.

In these notes are illustrated the more common changes which are now known to be caused by these organisms. In order to interpret correctly the results obtained, it is necessary to know the normal composition of the materials in question. To determine this often involves analytical processes not strictly included under the head of sanitary tests, namely, the determination of total solids, ash, etc., and certain changes of sanitary significance not due to the lower forms of life, such as the vitiation of air by the burning of lights or the breathing of human beings. Sanitary chemistry may also properly include the examination of articles of food for the presence of adulterants or poisons.

It is evident that any classification of topics is only temporary and tentative in the present state of knowledge. Water analysis and air analysis are each treated in a separate section. In the former the products of bacterial action are to be most carefully studied and accurately determined, in order that the deductions from the results may be of value. Soil analysis has been fully described in works on agricultural chemistry (see *Bibliography*, page 28), and is therefore omitted. Food analysis is treated on the broad lines above indicated. A few typical substances only will be considered, and the methods of examination given will be such as to elucidate the scientific aspect rather than technical detail of the subject. Both on account of its importance as a food stuff and on account of its availability for the tests, MILK has been chosen as a type of animal food. This class

includes meats and meat products, meat tablets, peptones, and other prepared animal foods. The same methods of examination may be applied to the analysis of fertilizers.

The analysis of milk includes the determination of specific gravity, water or total solids, ash, fat, nitrogen, sugar, together with the separation of casein and albumen, the determination of the products of putrefaction and fermentation, namely, ammonia and acidity, also the detection of preservatives and coloring matters.

Wheat is taken as a type of vegetable food. This class includes macaroni, gluten, bread, beans, bananas, etc. Determinations are also made of water or total solids, ash, fat, nitrogen, starch, cellulose, and the products of peptonization and saccharification.

The results of fermentation are illustrated by the determination of alcohol in beer, wine, meat extracts, patent medicines and "temperance drinks," flavoring essences, etc.

The determination of the specific gravity and "extract" is also sometimes desirable.

The nature and composition of butter and other animal fats, of olive and cottonseed oil, with tests for the identification of each, are also briefly considered.

Condiments, spices, tea, and coffee are largely identified by microscopic tests, but adulterations of these, as of most common groceries, affect the health less than the pocket. Text-books on food adulterations furnish sufficient information on these points. (See *Bibliography*, page 28.)

## MILK ANALYSIS.

*General Statements.* — Milk is an emulsion of fat globules with casein and other albuminoids, mineral matters probably in combination, sugar and water.

Dr. Vieth gives for the year 1890 the average of 22,670 samples and for eleven years the average of 120,540 samples, as follows:

| | Average, 1890 | Average of eleven years. |
|---|---|---|
| Specific gravity | 1.0322 | ..... |
| Total solids | 12.84 | 12.90 |
| Solids not fat | 9.10 | 8.80 |
| Fat | 3.74 | 4.10 |

The solids not fat are composed of —

| | |
|---|---|
| Milk sugar, | 4.91 |
| Proteids, | 3.27 |
| Mineral matter or ash, | .70 |
| | 8.88 |

An examination of milk as regards its healthfulness usually consists in determining what changes, if any, have taken place in its constituents due to the growth of microörganisms, for which it affords a most inviting culture medium. These changes are termed fermentations. The two most common are the acid and the alkaline.

Acid Fermentation. — Milk sugar yields lactic acid under the influence of a class of organisms of which *bacillus acidi lactici* is one. The extent to which this change has taken place is shown by the test for acidity.

Alkaline Fermentation. — Albumen and casein are decomposed with the formation of ammonia and other intermediate nitrogenous products, some of them of a poisonous character, as is shown by the prevalence of cholera infantum when such decomposed milk is used, and by cases of poisoning by ice cream, etc. The fat becomes in time rancid, perhaps by butyric fermentation, but this change takes place, as a rule, more slowly, and is not as common as the others.

Alcoholic Fermentation. — The production of koumiss is an instance of an artificially incited change. There are various other occasional fermentations which cause a slimy appearance or a bitter taste or the production of butyric acid. The student is referred to the various journals for accounts of these. The United States Department of Agriculture has recently published Bulletin No. 25, on *Dairy Bacteriology*, by H. W. Conn.

The examination of milk for the detection of adulteration is confined to certain physical tests, and to the determination of water, fat, sugar, and ash, and the detection of harmful preservatives. In all manipulations with milk the importance of thorough and frequent *mixing*, *not shaking*, cannot be too strongly emphasized; this is best accomplished by pouring it from one vessel to another. The apparatus used in containing and measuring milk should be thoroughly washed out as soon as possible.

## PHYSICAL TESTS.

*Specific Gravity.* — This is taken in the usual manner by a hydrometer or by the Westphal balance. The temperature should not vary more than two degrees from 15° C. A reading of the lactometer, a standard often used, and dependent upon average specific gravity, is also to be taken at the same time.

*Fat.* — This is estimated by Feser's lactoscope, the *modus operandi* of which is given with that instrument. It is based upon the opacity of the milk. Another instrument of like principle is the pioscope of Professor Heeren (*Repit f. Anal. Chem.*, 1881, p. 247), which consists of an ebonite disk with a raised rim; a few drops of milk are brought upon it, the painted glass cover placed over it, and the color of the milk matched with one of those on the cover.

*Cream.* — The creamometer, an elongated test tube with graduations near the top, is filled to the zero mark with the milk, and allowed to stand twenty-four hours, after which the percentage of cream is read off. The rapidity with which the cream rises indicates whether sodium carbonate has been added, its action being to retard the rise of cream. Should the cream separate very quickly and the milk be blue, the indication is that water has been added or that the milk is of poor quality. In the municipal laboratory at Amsterdam a few drops of a strong solution of methyl violet are added to render the reading sharper, as it does not dissolve appreciably in the cream. Cream contains the most of the fat of milk, with a small proportion of the other constituents. One thousand and ten samples of cream gave an average of 48.3 per cent. fat. Skimmed milk, from centrifugal separators, yields from 0.2 to 0.4 per cent. fat. If convenient, a *microscopical examination* should be made; this will show the fat present as an infinite number of minute globules of various sizes, there being two or three million per cubic millimeter.

## CHEMICAL TESTS.

*Reaction.* — Normal milk gives the amphioteric reaction, *i. e.*, turns delicate litmus both red and blue; it ultimately becomes acid.

*Acidity.* — This is due to the fermentation of milk sugar and the production of lactic acid. The degree of acidity is determined by the titration of 5 cc. of milk (previously diluted with 50 cc. of water) by a solution of tenth normal sodium hydrate, using phenol-phthalein as an indicator. The acidity may be expressed in cubic centimeters of sodium hydrate, or each tenth of a cubic centimeter may be considered as a degree of acidity. For example, six hours after milking the acidity may

be fourteen to twenty-five degrees; forty-eight hours after milking it may reach one hundred degrees. When the acidity reaches twenty-three degrees milk coagulates on boiling. (*Analyst*, vol. xvi, p. 200.) An example of the rate of change is given in the following table:

| Day. | Acidity. cc. | Sugar. Degrees of rotation. |
|---|---|---|
| 1 | 2.2 | 25.2 |
| 2 | 5.5 | 23.1 |
| 3 | 11.0 | 21.6 |
| 6 | 13.2 | 14.2 |
| 7 | 15.0 | 9.4 |
| 8 | 16.3 | 7.8 |
| 9 | 17.2 | 1.2 |

"*Thesis*," *Ethel B. Blackwell, M. I. T., 1891.*

*Alkalinity or Ammonia.* — The nitrogenous constituents of milk are also subject to fermentation or decomposition by means of the growth of bacteria. Ammonia (or a substance which yields ammonia on distillation) is formed, and tends to neutralize the lactic acid. On the other hand, abundant acid tends to check the growth of the alkaline ferments. It depends upon certain conditions of seeding and of temperature which gets the best start in the race. It is to the alkaline fermentation that most of the danger in using unsterilized milk is due.

### DETERMINATION OF ALKALINITY OR AMMONIA.

#### APPARATUS REQUIRED.

25 cc. pipette; Kjeldahl distilling flask; 250 cc. receiving flask; 2 burettes.

#### CHEMICALS REQUIRED.

Sodium carbonate; sulphuric acid 1 : 40; $\frac{N}{10}$ hydrochloric acid; $\frac{N}{10}$ sodium hydrate; phenolphthalein 1 : 500 in 90 per cent. alcohol.

25 cc. of the milk to be tested are delivered from a pipette into a Kjeldahl distilling flask. 350 cc. ammonia free water and .5 gram sodium carbonate are added. About 200 cc. are then distilled into a 250 cc. receiving flask containing about 20 cc. sulphuric acid 1 : 40. This distillate is redistilled, with the addition of .5 gram sodium carbonate, or enough to neutralize the acid present, in order to convert into ammonia any amines formed during the first distillation; or enough alkaline permanganate to give a decided pink color may be used instead of the sodium carbonate. The distillate is received into 15 cc. of $\frac{N}{10}$ hydrochloric acid and titrated with $\frac{N}{10}$ sodium hydrate. Phenolphthalein is used as an indicator.

## TOTAL SOLIDS.

### *Wanklyn's Method.*

APPARATUS REQUIRED.

Shallow platinum dishes of about five square inches bottom area (blacking box covers answer very well); 5 cc. burette pipette; beakers.

The shallow platinum dish is weighed and left on the balance pan; 5 grams are added to the weights upon the other pan, and 5 cc. of the well-mixed milk, measured from the burette pipette, are delivered into the dish, and the whole weighed as rapidly as possible, the movement of the rider probably sufficing. The milk is evaporated to dryness upon a water bath, and dried at 100° to a constant weight. Dr. Davenport dries at 105°; Wanklyn recommends drying three hours each time, and not weighing a second time; and Gerber advises coagulation by absolute alcohol before evaporation.

REFERENCES.

Wanklyn, *Milk Analysis.*
Gerber, *Milch Analyse.*

## FAT.

### 1. *Wanklyn's Method.*

APPARATUS REQUIRED.

As in total solids, pincers; gasolene wash bottle; glass rods.

CHEMICALS REQUIRED.

Gasolene, sp. gr. 86° B., which leaves no residue.

The dried and weighed residue from the determination of total solids is treated in a warm place with gasolene. After about fifteen minutes the gasolene is decanted off and the residue treated with a fresh portion. Six portions will suffice. Finally the dish is held with the pincers and the outside and rim carefully washed off by a stream of gasolene from the wash bottle, to insure the removal of all the fat. The residue is dried and weighed, and the difference between this weight and the original is the weight of the fat. The results are about 0.2 per cent. lower than those obtained by other methods, as the fat is not in a condition to be readily extracted.

REFERENCE.

Davenport, *Mass. State Bd. of Health Rep't*, xviii, 1886, p. 139.

### 2. *Adams' Method.*

APPARATUS REQUIRED.

Return flow condenser; Soxhlet's extractor; wide-mouthed 100 cc. flasks; large beaker for a water bath (if a special bath is not at hand); 5 cc. pipette; extracted filter paper in strips 22 inches long by $1\frac{3}{4}$ inches wide.

CHEMICALS REQUIRED.

Gasolene, sp. gr. 86° B., which leaves no residue.

Absorbent paper exercises a selective action on the constituents of milk, so that the fat is left on the surface of the paper mixed with only about one third of the non-fatty solids, and hence it is more easily extracted. The strip of paper may be pinned by one corner, so as to hang free; 5 cc. of the milk to be tested are run on to the upper end from a pipette. When dry the paper is carefully rolled into a coil, placed in the extractor, and treated with gasolene for about two hours; or the coil may be made first, and the milk run on to it. The flask, previously tared, is weighed after the evaporation of the gasolene, and the increase in weight is the fat.

### 3. *The Babcock Method.*

The fat is freed from the other constituents and collected in the graduated neck of the bottle for measurement.

APPARATUS REQUIRED.

Centrifugal machine; whirling bottles; 17.6 cc. pipette; 17.5 cc. graduate; wash bottle containing boiling water.

CHEMICALS REQUIRED.

Sulphuric acid, 1.835 sp. gr.

17.6 cc. of the milk to be tested are delivered from a pipette into a long-necked graduated whirling bottle. 17.5 cc. sulphuric acid, 1.835 sp. gr., are gradually added, with vigorous shaking after each addition of acid. The sulphuric acid should blacken the milk and cause a considerable amount of heat. After the acid is added and before the bottles are allowed to cool they should be whirled. They are to be placed in opposite pockets, in even numbers, and whirled for six to seven minutes, the large wheel making eighty to ninety revolutions per minute. The bottles are then removed, and the hot water, which should be ready by this time, is added to each bottle until the surface of the

mixture rises nearly to the top of the graduations on the neck. The bottles are again placed in the whirler, and turned at about the same rate for one minute. At the end of this time the bottles can be taken out and the length of the column of fat measured by dividers, one point of which is placed at the bottom and the other at the upper limit of the fat. If one point of the dividers is then placed at the zero mark of the scale on the bottle used, the other will be at the per cent. of fat in the milk examined.

### RELATION BETWEEN SPECIFIC GRAVITY, FAT, AND SOLIDS IN MILK.

The specific gravity of milk is, in the main, a function of two factors, namely, the percentage of solids not fat and that of the fat. The former raises it; the latter lowers it. Taken by itself it affords very little indication of the composition, but if any other item be known it should be possible to find, by calculation, the other quantities, provided the assumption is true. The solids not fat are made up of several fluctuating constituents, but "normal milk" seems to contain them in such a constant ratio that a calculation serves at least to detect an abnormal sample.

| | Of fat. | Of casein and albumen | Of sugar. | Of ash. |
|---|---|---|---|---|
| Specific gravity . . . . | .93 | 1.34 | 1.65 | 3.0 |

| | Ash. | Proteid. | Sugar. |
|---|---|---|---|
| Ratio in normal milk . . . . . | 2 | 9 | 13 |

### EXAMPLE.

Given the specific gravity and solids, to calculate the fat:

Specific gravity $= Gr$. The amount which each per cent. of solids not fat raises the specific gravity $= s$. The amount which each per cent. of fat lowers the specific gravity $= f$. Total solids $= T$. Solids not fat $= S$. Fat $= F$. $Gr = Ss - Ff$; or, substituting for $S$ its value $T - F$, $Gr = (T - F)s - Ff$. The uncertainty of the calulation lies in the values of $s$ and $f$, which have not been quite satisfactorily determined.

The simple formula $\frac{6}{5}F = T - \frac{G}{4}$ answers within the limits of experimental error for normal milk, but not for skimmed or watered milk.

Data: $Gr = 1.0323$. $G = Gr - 1 \times 1000 = 32.3$. $T = 12.90$.

$$\frac{6}{5}F = 12.90 - \frac{32.3}{4} = 4.02$$

Calculated. Found.
4.02 3.99.

A similar relation has been worked out for the proteids and sugar, so that from three determinations the whole composition may be calculated. Example as above:

Ash $= .70 = A$. Formula $P = 2.8T + 2.5A - 3.33F - .68\frac{G}{Sp.Gr}$,

or, $P = 36.12 + 1.75 - 13.32 - 21.28 = 3.27$.

Sugar $= T - (A + P + F)$.
Sugar $= 12.90 - (.70 + 3.27 + 4.02) = 4.91$.

CHIEF REFERENCES.

*Analyst*, vol. vii, p. 129.
*Analyst*, vol. xiii, pp. 26 and 49.

*With Chart.*

*Analyst*, vol. xv, p. 170.
*Analyst*, vol. xvii, p. 169.
*Analyst*, vol. xx, pp. 7 and 57.

## SUGAR.

### 1. *By Titration with Fehling's Solution.*

APPARATUS REQUIRED.

Pipettes 25 cc. and 5 cc., also 1 cc. divided into hundredths; 50 cc. graduate; 250 cc. bottle; 500 cc. graduated flask; burettes; thermometers; water bath; beakers; 4-inch casserole or a 6-inch porcelain dish; funnels; folded filters; medicine dropper; extra small filters.

CHEMICALS REQUIRED.

69.28 grams C. P. copper sulphate to 1 liter water; 346 grams sodium potassium tartrate and 80 grams sodium hydrate in 1 liter; acetic acid, 25 per cent. solution; potassium ferrocyanide, 1:50 made the day it is to be used; aluminum hydrate, as used for chlorine in water. See notes on Water Analysis.

Any method of clarification may be used. The following answers very well.

25 cc. of milk are measured into a 250 cc. bottle; 15 cc. of aluminum hydrate, 75 cc. of hot water, and 0.5 cc. of acetic acid (25 per cent. solution) are added. The bottle is tightly stoppered, shaken vigorously, and

placed on its side to allow the precipitate to settle, after which the almost clear liquid is decanted into a beaker. The precipitate in the bottle is washed three times with hot water, by decantation, the washings being poured into the beaker. The contents of beaker and bottle are then thrown upon a 6-inch filter, and the precipitate is washed until the volume of the filtrate reaches 500 cc.

*Titration.* — 5 cc. of the copper solution and 5 cc. of the alkaline tartrate are accurately measured out into the 4-inch casserole or 6-inch porcelain dish, diluted with 40 cc. of water, and heated to boiling. The whey as above prepared is added from a burette as long as a blue color is seen in the liquid, which must be kept *constantly boiling and made up to 50 cc.* When the end-point is nearly reached a test for copper should be made in the solution. To this end a few drops of the liquid are run from a medicine dropper through a very small filter into a test-tube, or on to a porcelain plate, containing a dilute solution of potassium ferrocyanide strongly acidulated with acetic acid, when, if copper be present, the characteristic rose coloration will appear. This will give the approximate number of cubic centimeters required to decolorize the copper solution.

The exact number may be most conveniently found by adding the quantity of whey above used to a fresh portion (10 cc.) of Fehling's solution and 40 cc. of water, boiling exactly two minutes, filtering the whole through a 4-inch filter, and testing the filtrate as above described.

If copper be still present, the operation is repeated with 0.2 cc. more whey until the end-point is reached; or, if the drop of solution be colorless, 0.2 cc. less of the whey is used each time until copper appears. If 10 cc. of Fehling's solution of the strength given are reduced by 0.067 gram of milk sugar, then $\frac{500 \times .067}{\text{No. cc. whey used}} =$ grams of milk sugar in 25 cc. of the milk. The results are reported in per cent. From 27 to 33 cc. of whey are usually required to reduce 10 cc. of Fehling's solution. A standardization of the reagent with pure milk sugar should be made.

The cuprous oxide formed may be filtered off, washed, dissolved in nitric acid, and the copper determined by the battery, in which case larger quantities may be employed.

REFERENCES.

Colby, *New York State Bd. of Health Rep't*, 1882, p. 611.
Beckmann, *Fres. Zeit.*, xxv, 529.
Beckmann, *The Analyst*, xi, 235.

### 2. *By the Saccharimeter.*

The necessary clarification is made either with basic lead acetate, acid mercuric nitrate, or mercuric iodide, and the resulting whey polarized. (See Bulletin No. 28, U. S. Department Agriculture, p. 208, 1890.)

#### NITROGENOUS MATTERS — CASEIN, ALBUMEN, ETC.

5 grams of milk are used and treated as in the notes upon the "Determination of Nitrogen by the Kjeldahl Process," which see.

#### ASH.

The residue in the platinum dish from the extraction of fat according to Method 1 is ignited at a low red heat.

#### ADULTERANTS.

*Water.* — The presence of nitrates indicates that the milk has been watered. Uffelman (*The Analyst*, x, 146) recommends the following method for their detection. Diphenylamine the size of half a pea is dissolved in 25 drops sulphuric acid in a 3 inch porcelain dish. A few drops of the suspected milk are allowed to trickle down the sides of the dish, when, if nitrates be present, at the point of meeting a bluish stripe will form and ultimately tint the whole mixture. The picric acid method (see notes on Water Analysis) may also be used.

### *Determination of Water Added to Milk.*

For a quantitative estimation of the amount of added water Radliscu (*Mitth. a. d. pharm. Inst. u. Labor. d. Univ. Erlangen, Hilger, Heft*, iii, pp. 93–112) recommends the determination of the specific gravity of the whey, or "serum," as he terms it.

#### APPARATUS REQUIRED.

100 cc. pipette; 2 cc. pipette; beakers; funnels; water bath; thermometer; filters; Westphal balance.

#### CHEMICALS REQUIRED.

Acetic acid, 25 per cent. solution.

100 cc. of the milk are thoroughly mixed in a beaker with 2 cc. of the acetic acid, and heated in a water bath at 85° C. for five to ten minutes. The casein is by this treatment precipitated as a compact cake, and is easily filtered off. The contents of the beaker are now filtered, care being taken to bring as little of the precipitate upon the

filter as possible; the filtrate, carefully mixed, is cooled to 15° C., and its specific gravity taken by the Westphal balance. Radliscu finds that the specific gravity of the whey or serum in a normal milk is never below 1.027, that it contains 6.3 to 7.5 per cent. total solids, of which .22 to .28 per cent. are fat. The addition of each 10 per cent. of water lowers the specific gravity by .0005 to .0010, and the percentage of total solids from 0.3 to 0.5 per cent.

### OTHER SUBSTANCES.

*Salt.* — Detected by the high percentage of ash, and determined volumetrically by silver nitrate after clarification with alumina.

*Cane Sugar.* — Detected by the polariscope.

*Starch.* — 5 cc. of the milk warmed in a small beaker are treated with a few drops of iodine solution when the characteristic blue color indicates starch.

*Nitr.* — Detected in the ash.

### COLORING MATTERS.

Annatto, caramel, and carrot extract are the substances usually employed to color watered milk. Thoms (*Pharm. Zeit.*, xxxii, 59) found ultramarine in milk.

*Annatto.* — Dr. Davenport (*Mass. State Bd. of Health Rep't*, xvi, 140) recommends the following method: A strip of filter paper is placed in the milk to be tested, previously made alkaline with carbonate of soda, and after being allowed to remain twelve hours is washed out. If annatto be present it will have acquired a salmon or light copper tint. This color is changed by sulphuric acid to dark blue; by stannous chloride to a pink.

*Caramel.* — See *Fres. Zeit.*, xxiv, 30; *The Analyst*, x, 36.

For other coloring matters see Leeds, *The Analyst*, xii, 150.

### PRESERVATIVES.

*Salicylic Acid.* — A few drops of ferric chloride are added to 5 cc. of the milk. Should salicylic acid be present, a dirty purple to violet coloration is produced.

*Formalin or Formic Aldehyde.* — This has recently come into use; the odor usually betrays it. (*Chem. News*, vol. lxxi, page 247.)

*Boric Acid.* — Hilger (*Nahr. und Genussmittelu*) recommends the following process: Five drops calcium hydrate are added to 10 (or 100) cc.

of the milk and evaporated to dryness on a water bath. The residue is charred, a few drops of water are added, the liquid is made slightly acid with hydrochloric acid, and filtered into a porcelain dish. The usual qualitative test with alcohol or turmeric paper is applied. (See also Kretschmar, *The Analyst*, xii, 159.)

*Benzoic Acid.* — *Fres. Zeit.*, xxi, 531 ; *Jour. Anal. Chem.*, ii, 446.

*Carbonate of Soda.* — Detected in the ash.

*Hydrogen Peroxide.* — See Hilger, *loc. cit.*, p. 58. See also Stokes, *The Analyst*, xvi, 123.

## BUTTER ANALYSIS.

*General Statements.* — Butter consists of the fat of milk, together with a small percentage of water, salt, and curd; these exist in about the following proportions:

| | | | |
|---|---|---|---|
| Fat, | 78.00–90.0 per cent.; | average, 82 | per cent. |
| Water, | 5.00–20.0 " " | " 12 | " " |
| Salt, | 0.4 –15.0 " " | " 5 | " " |
| Curd, | 0.11– 5.3 " " | " 1 | " " |

The fat consists of a mixture of the glycerides of "the fatty acids," which, when saponified, yield an increased weight of product, owing to the combination of water in the process. One sample gave 106.32 parts from one hundred parts of fat containing 12.5 per cent. of glycerine. (For further discussion see *Analysis and Adulteration of Food*, James Bell. On the constitution of butter fat see *Analyst*, vol. xvi, p. 161.)

The fatty acids have a very complex composition, not yet perfectly understood. The Danish chemist Koefoed gives the following as the proportion of the acids thus far isolated:

| | | Per cent. |
|---|---|---|
| Oleic acid, | $C_{17}H_{33}COOH$ | 34.0 |
| Acid of the formula, | $C_{15}H_{28}O_4$ | |
| Acid of the formula, | $C_{29}H_{54}O_5$ | |
| (The latter is probably a mixture.) | | |
| Stearic acid, | $C_{17}H_{35}COOH$ | 2.0 |
| Palmitic acid, | $C_{15}H_{31}COOH$ | 28.0 |
| Myristic acid, | $C_{13}H_{27}COOH$ | 22.0 |
| Lauric acid, | $C_{11}H_{23}COOH$ | 8.0 |
| Capric acid, | $C_9H_{19}COOH$ | 2.0 |
| Caprylic acid, | $C_7H_{15}COOH$ | 0.5 |
| Caproic acid, | $C_5H_{11}COOH$ | 2.0 |
| Butyric acid, | $C_3H_7COOH$ | 1.5 |

*Analyst*, vol. xvii, p. 130.

The examination, from a sanitary standpoint, consists in the determination of the quantity and condition of the curd and in the test for gelatin, since it is probably only in the possible decomposition of the nitrogenous portion that danger to health lies. It is now well recognized that the addition of oleomargarine is not injurious to health. It has become, however, a not infrequent practice to secure an admixture of a large per cent. (as high as 33 per cent.) of curd or other nitrogenous material in certain fresh butters. If this mixture is eaten at once there is no danger; but on keeping, a decomposition occurs which is liable to produce serious effects. The percentage composition of the butter has, therefore, a sanitary as well as an economic aspect.

The "aroma" of butter seems to be connected with the decompositions caused by the growth of bacteria on the sugar and casein, and not by a change in the fats; but there is no evidence that any unwholesome effect is produced.

The usual examination consists in the determination of fat, water, salt, and curd.

### EXAMINATION OF THE FAT.

The butter fat is isolated, saponified, and the volatile fatty acids are determined by distillation and titration, as in the Reichert method; or they are washed out and the fixed fatty acids weighed, as in the Hehner method; or the weight of iodine required to saturate the acids is found by the Hübl method.

#### APPARATUS REQUIRED.

Tall 30 cc. beakers; pipette with bulb, graduated to deliver 5.75 cc. water; 250 cc. round-bottomed flasks; 110 cc. graduated flasks; 100 cc. graduated flasks; 100 cc. graduated cylinder; beakers; funnels and filters.

#### CHEMICALS REQUIRED.

Absorbent cotton; sulphuric acid 1 : 40; potassium or sodium hydrate 1 : 1; 95 per cent. alcohol redistilled from potassium hydrate; $\frac{N}{10}$ sodium hydrate; $\frac{N}{10}$ barium hydrate; phenolphthalein 1 : 500 in 90 per cent. alcohol; bits of ignited pumice dropped while hot into water and bottled for use.

*Procedure.* — A piece of butter — about a cubic inch — is melted in a small narrow beaker placed in the water bath. After about fifteen minutes, during which time the temperature should have risen not above 60° to 70°, the water, salt, and curd will have settled to the bottom, and the clear fat may be decanted into a similar beaker through absorbent cotton or asbestos, care being taken that none of the water or curd is

brought upon the filter. When the filtered fat has cooled to about 40° the pipette is placed in the beaker and the whole weighed.

By means of the pipette about 5 grams of fat are transferred to a dry 250 cc. round-bottomed flask, the pipette replaced in the beaker, and the whole again weighed. The difference in weight gives the exact quantity of fat taken. It is a saving of time, if several portions are to be weighed out, to make the weights one after the other, so that one weight will suffice for a determination. Weigh off thus: Two portions of 5 grams each into the round-bottomed flasks for Reichert's method, a portion of 2.5 to 3 grams into a 500 cc. beaker for Hehner's process, two portions of about a gram each into 300 cc. bottles for Hübl's process.

### 1. *Reichert-Meissl Number for Volatile Fatty Acids.*

To the fat in the 250 cc. round-bottomed flasks are added 2 cc. of the caustic potash and 10 cc. of 95 per cent. alcohol. (The addition of 3 cc. ether, and then a vigorous boiling, reduce the time of saponification to a few minutes, or even seconds.) The flasks are then connected with long, straight glass tubes, serving as return flow condensers, and placed upon the water bath until saponification is complete; frequent shaking hastens the process. When this has taken place the flasks are disconnected and the alcohol evaporated. After the complete removal of the alcohol, 100 cc. of boiled distilled water, at a temperature of about 50°, are slowly added from a graduate, and the soap dissolved by gently warming on the water bath. Rapid addition of water may decompose the soap, setting free the fatty acids:

$$C_{17}H_{35}COOK + H_2O = C_{17}H_{35}COOH + KOH.$$

When the solution of soap has cooled to 60° or 70°, it being perfectly clear, 50 cc. of the dilute sulphuric acid are added to set free the fatty acids. Two bits of pumice are dropped into the flask, which is then closed by a cork tied in with twine and immersed in boiling water until the fatty acids have melted to an oily layer floating on the top of the liquid. It is then cooled to 60°, the cork removed, and the flask attached to the condenser.

The distillation should be so conducted that 110 cc. come over in thirty minutes.

The distillate, after being thoroughly mixed, is poured through a dry filter, and 100 cc. are titrated with $\frac{N}{10}$ barium or sodium hydrate, using phenolphthalein as an indicator. The number of cubic centime-

ters of alkali used is increased one tenth, and the weight of fat corrected for any number greater or less than 5 grams.

For example, if 5.3 grams butter fat are used, and 100 cc. of the distillate require 27.4 cc. $Ba(OH)_2$, 110 cc. would require $27.4 + 2.74 = 30.14$ cc. Then $5.3 : 30.14 :: 5 : x$. $x = 28.4$.

$x$ is the Reichert-Meissl number. Butters which give a number over 27 and under 30 may be considered genuine. Those which give a number between 25 and 27 are somewhat doubtful, and those which give less than 25 should be looked upon with suspicion.

| | French Butter. | | English Butter. |
|---|---|---|---|
| | Fresh. | Salt. | Salt. |
| Fat | 84.39 | 83.44 | 82.98 |
| Water | 13.98 | 12.86 | 13.99 |
| Solids not fat | 1.51 | 1.63 | 0.89 |
| Salt | .12 | 2.07 | 2.14 |
| Reichert number | 29.1 | 29.1 | 28.1 |

REFERENCES.

Meissl, *Dingler polyt. Jour.*, ccxxxi, 478.
" *Zeit. Anal. Chem.*, xviii. 63.
Sendtner, *Archiv. für Hygiene*, i, 137; viii, 424.
Wollney, *Analyst*, xii, 203; xiii, 8.

## 2. *Hehner's Method for Direct Determination of the Fixed Fatty Acids.*

APPARATUS REQUIRED.

500 cc. beakers; funnels; "weighing beakers;" filters dried over sulphuric acid.

CHEMICALS REQUIRED.

Potassium hydrate as in 1; hydrochloric acid, 1.12 sp. gr.; 95 per cent. alcohol.

The portion of 2.5 grams weighed out into the 500 cc. beaker is saponified by using 1 cc. potassium hydrate diluted with 20 cc. 95 per cent. alcohol. As it is not essential to prevent the escape of the volatile acids, the precautions in Method 1 are unnecessary, but loss by spurting must be avoided.

The aqueous solution of the soap, which should be 300 to 400 cc., is decomposed by 10 cc. hydrochloric acid and heated in a water bath almost to boiling until the clear oil floats. The beaker and contents are allowed to become quite cold; the clear liquid, and finally the solid fats, are brought upon the thick weighed filter. When the beaker and fat are

well washed with cold water, the adhering fat is washed out with boiling water, which is poured through the filter, taking care that the filter is never more than two thirds full. The funnel is cooled by plunging it into cold water, the filter removed, placed in a weighing beaker dried at 100° and weighed as soon as practicable, since long heating causes oxidation. A weight constant within 2 mgs. is sufficiently accurate.

Eighty-seven and one half per cent. is usually taken as the proportion of fixed fatty acids in butter; 88 and 89 per cent. have been frequently found. All other fats yield from 95 to 96 per cent. insoluble fatty acids.

REFERENCES.

*Butter, its Analysis and Adulteration*, Hehner and Angell.
Dietzell and Kresner, *Fres. Zeit.*, xviii, 83.
Heintz, *Fres. Zeit.*, xvii, 160.
Hehner, *Fres. Zeit.*, xvi, 149.

### 3. *Method of Baron Hübl.*

This depends upon the fact that certain of the fatty acids, notably the "unsaturated acids," as oleic acid, $C_{17}H_{33}COOH$, take up the halogens with the formation of addition-products.

APPARATUS REQUIRED.

300 cc. glass-stoppered white glass bottles; glass-stoppered burettes; graduates.

CHEMICALS REQUIRED.

25 grams iodine in 500 cc. 95 per cent. alcohol; 30 grams mercuric chloride in 500 cc. 95 per cent. alcohol; the two are mixed, and after standing 24 hours are filtered; $\frac{N}{10}$ sodium thiosulphate (24.6 grams to 1 liter); starch paste 1 : 200; potassium iodide 150 grams to 1 liter; potassium bichromate C. P. 3.874 grams to 1 liter; strong hydrochloric acid; chloroform.

The butter fat, weighed into the 300 cc. bottles, is dissolved in 10 cc. of dry chloroform. About 30 cc. — in the case of a doubtful butter 50 cc. — of the iodo-mercuric solution are accurately measured from a glass-stoppered burette, and the bottle is allowed to stand, with frequent shaking, for three hours in a dark closet. About 100 cc. of distilled water, with 20 cc. potassium iodide, are then added — the latter for the purpose of keeping in solution mercuric salts — and the excess of iodine uncombined with fat is titrated with $\frac{N}{10}$ thiosulphate. When the solution has become faintly yellow, a few drops of freshly prepared starch solution are added and the titration continued to disappearance of the blue color.

The results are calculated in grams of iodine absorbed by 100 grams of fat. This is frequently called the Hübl or Iodine absorbtion number.

*Standardization of the Iodo-Mercuric Solution.* — Since the strength of this solution is liable to change, the relation between it and the thiosulphate should be determined by carrying through a blank in the same manner and with the same quantities of reagents as in the case of the fat.

*Standardization of the Thiosulphate Solution.* — As this is not permanent, its strength should be determined by means of the standard solution of potassium bichromate, 1 cc. of which liberates 0.01 gram of iodine.

About 20 cc. of potassium bichromate are accurately measured from a burette into a 300 cc. glass-stoppered bottle, 10 cc. of potassium iodide and 5 cc. strong hydrochloric acid added, and the iodine which is set free is titrated with thiosulphate as above directed:

$$K_2Cr_2O_7 + 14HCl + 6KI = 8KCl + Cr_2Cl_6 + 7H_2O + 6I.$$

CALCULATION OF RESULTS — EXAMPLE.

STANDARDIZATION OF THIOSULPHATE SOLUTION.

17.2 cc. thiosulphate = 21.5 cc. bichromate = 0.215 gram iodine.
1 cc. thiosulphate = 0.0125 gram iodine.

STANDARDIZATION OF IODINE SOLUTION.

31 cc. iodine solution = 46.5 cc. thiosulphate.
1 cc. iodine solution = 1.5 cc. thiosulphate.

If 31 cc. iodine solution have been added to 1.049 grams of fat, then $31.0 \times 1.5 = 46.5$ cc. is the equivalent amount of thiosulphate solution; and if 19.4 cc. thiosulphate were used to titrate excess of free iodine, $46.5 - 19.4 = 27.1$ cc. is the amount of thiosulphate equivalent to iodine combined with the fat. Then since 1 cc. thiosulphate is equivalent to 0.0125 free iodine, $\frac{27.1 \times 0.0125}{1.049} \times 100 = 32.29$ grams of iodine combined with 100 grams fat.

It is assumed that 100 grams pure butter absorb 30 to 40 grams iodine; artificial butter, 55 grams; oleomargarine, 63 to 75 grams; olive oil, 83 grams; and cottonseed oil, 106 grams.

REFERENCES.

Hübl, *Dingler polyt. Jour.*, ccliii, 281.
*Jour. Soc. Chem. Ind.*, iii, 641.
Pattinson, *Jour. Soc. Chem. Ind.*, viii, 30.
Williams, *The Analyst*, xiv, 103.
Hehner, *The Analyst*, xx, 49, 176, 280.

### PHYSICAL METHODS.

*Microscopic Examination.* — The student is referred to Bulletin No. 13, U. S. Dept. of Agriculture, Part I, pp. 29–40; Part IV, pp. 449–455.

*Specific Gravity.* — This is most conveniently determined at 100° C. by means of the Westphal balance (see Allen, *The Analyst*, xi, 223; also the Bulletin, Part IV, pp. 430–431.) The pyknometer method is, however, the one adopted by the Association of Official Agricultural Chemists, to whose report (Bulletin No. 28, 1890, p. 196) reference is made.

*Melting Point.* — This is best determined according to the directions given in the Bulletin just mentioned, p. 198.

*Refractive Index.* — See Bulletin No. 28, p. 207.

### DETERMINATION OF WATER.

About 2 grams of butter are weighed in a shallow dish having a flat bottom two inches in diameter and containing a slender stirring-rod two and a half inches long. The butter is heated in the oven at 100° C. for thirty minutes, cooled in a desiccator, and weighed. It is then heated again for periods of fifteen minutes, and weighed until the weight remains constant. During the process of heating the butter should be frequently stirred, to hasten evaporation of the water. The loss in weight is calculated as water, although a portion of the volatile acids is also lost, the amount depending upon the time of heating.

### DETERMINATION OF SALT.

10 grams of the butter are weighed in a small beaker, 30 cc. of hot water added, and, when the fat has completely melted, the whole transferred to a separatory funnel. The contents are thoroughly shaken, the fat allowed to rise to the top, and the water drawn off. 30 cc. of water are again added, and the operation repeated until washings are obtained which give but a faint turbidity when tested with silver nitrate. The washings are thoroughly mixed, made up to 250 cc., and 25 cc. titrated for chlorine in a six-inch porcelain dish, using $\frac{N}{20}$ silver nitrate with potassium chromate as an indicator.

### DETERMINATION OF CASEIN.

Estimated by Kjeldahl's process for the determination of nitrogen.

### DETECTION OF COLORING MATTERS.

5 grams of the filtered butter fat are dissolved in a separatory funnel in 25 cc. of ether; 25 cc. of water, rendered faintly alkaline with

sodium hydrate, are now added, and the mixture thoroughly shaken. The water dissolves the coloring matter, which may be investigated according to the directions for coloring matter in milk.

REFERENCES.

Martin, *The Analyst*, x, 163.
Moore, *The Analyst*, xi, 163.

APPROXIMATE DETERMINATION OF WATER, SALT, AND CURD.

*Hoorn's Method Modified.*

Place about 20 grams of butter in an open tube, and with a glass rod as a piston force the butter out into a test tube about 12 inches in length and 1 inch in diameter. Add 40 cc. gasolene, cork the tube securely, and shake vigorously; allow to settle, and siphon off the clear upper layer; add 40 cc. more gasolene, and repeat. Wash into the graduated Hoorn tube, allow the contents to settle, read off the amount of water and matters not fat.

REFERENCE.

Hoorn, *Fres. Zeit.*, xi, 334.

## FLOUR, PREPARED CEREALS, ETC.

This class of food stuffs is usually in a dry form and not liable to rapid change by micro-organisms, and the examination consists in the determination of their "food value." This may require a simple analytical process, as in the case of the quantity of nitrogen in a sample of "gluten" sold for diabetic patients, or in case of a brand of flour used in a hospital, or State institution. It may also require an estimation of the available food material, as in the case of two kinds of beans or corn. The actual determination of digestibility belongs rather to physiological than to sanitary chemistry.

TOTAL NITROGEN IN CEREALS AND OTHER ORGANIC SUBSTANCES CONTAINING COMBINED NITROGEN.

*By Kjeldahl's Process.*

APPARATUS REQUIRED.

Block tin condensers; 750 cc. round-bottomed flasks; 250 cc. flat-bottomed flasks; digestion flasks; graduates.

CHEMICALS REQUIRED.

Sodium hydrate (sp. gr. 1.31); $\frac{N}{10}$ hydrochloric acid; $\frac{N}{10}$ sodium hydrate; mercury; potassium sulphide, 40 grams to liter; methyl orange No. III, rosolic acid or cochineal; sulphuric acid, free from nitrogen.

*Principle.* — Oxidation of carbon and hydrogen, and conversion of organic nitrogen to ammonium sulphate by means of boiling sulphuric acid in presence of mercury, the latter acting as a carrier of oxygen, and being converted to mercuric sulphate. Precipitation of mercury by potassium sulphide to prevent the formation of mercur-ammonium compounds when the solution is made alkaline. Setting free of ammonia by neutralization of acid with sodium hydrate. Distillation of ammonia into a measured quantity of $\frac{N}{10}$ hydrochloric acid. Titration of excess of acid.

About 0.5 gram of the finely divided substance are transferred from a weighing tube to a digestion flask, 10 cc. strong sulphuric acid, free from nitrogen, and 0.2 gram metallic mercury added, and the flask is placed on a wire gauze under the hood. Gentle heat is applied until frothing has ceased and the liquid boils quietly. The flame is then increased and boiling continued until the solution becomes colorless. The flask is now allowed to cool for a minute, and a few crystals of potassium permanganate cautiously added, until the liquid has acquired a slight green or purple color. The condenser should at the same time be freed from ammonia by distillation with pure water, until a slight color only is given to 50 cc. of the distillate by Nessler's solution. About 25 cc. $\frac{N}{10}$ hydrochloric acid are carefully measured from a burette into a 250 cc. flask, and the condenser-tip placed beneath the surface of the liquid, a little water being added, if necessary, to seal it. About 100 cc. distilled water are now cautiously added to the liquid in the digestion flask, the whole transferred to a 750 cc. round-bottomed flask, and the former rinsed out with 100 cc. more water. Mercury is precipitated by the addition of about 20 cc. potassium sulphide, and finally 65 to 70 cc. sodium hydrate (sp. gr. 1.31) are carefully run down the side of the flask, in order, so far as possible, to avoid mixing with the acid liquid. If this precaution is neglected, ammonia may be lost. The flask is now connected with the condenser, and the contents thoroughly mixed by a gentle rotary motion. A low flame should be applied until the contents of the flask are thoroughly warmed, then increased until the liquid boils briskly, care being taken that none comes in contact with the cork. When 200 cc. have distilled over, the collecting flask is removed, after rinsing off the condenser-tip with distilled water, and the excess of acid titrated with $\frac{N}{10}$ sodium hydrate, using methyl orange or cochineal as indicator. Blanks should be carried through in the same way.

CALCULATION OF RESULTS.

If $a$ = no. cc. $\frac{N}{10}$ acid run into the small flask, $a'$ = no. cc. excess acid titrated, and $n$ = weight of nitrogen in sample, then $n = (a - a') \times .0014$.

To prevent bumping during distillation, a current of air, purified by passing through sulphuric acid, may be conducted into the liquid. If nitrates are present, see *Dept. Agric. Bull.* 43, p. 347.

## DETERMINATION OF STARCH.

In the absence of a satisfactory method for the determination of starch applicable in all cases, the student is referred to the standard works.

REFERENCES.

Maercker, *Handb. der Spiritusfabrikation*, p. 77 seq.
*U. S. Dept. Agric. Bull.* 43, p. 162.
Sadtler, *Indust. Org. Chem.*

The following method (Hibbard, *Jour. Am. Chem. Soc.*, xvii, 64) promises to be of use:

*Principle.* — Conversion of starch to dextrin and maltose by diastase in malt extract. Conversion of dextrin and maltose to dextrose by acid (hydrolysis).

The finely divided sample, which must contain 0.5 to 1.0 gram of starch, is placed in a flask with 50 cc. water, 3 cc. malt extract added, and boiled for one minute, with frequent shaking. The solution is then cooled to 60° C., 3 cc. malt extract added, and again heated slowly, so that fifteen minutes are required to reach the boiling point. It is then tested for starch by placing a drop upon a porcelain tile and adding a drop of solution of iodine in potassium iodide. Should a blue color appear, more malt extract must be added, and the boiling be repeated until all starch has been converted. The solution is then cooled, made up to 100 cc., and filtered through fine linen or cotton cloth. An aliquot part of the filtrate, 25 or 50 cc., is placed in a flask with 5 cc. hydrochloric acid (1.15 sp. gr.), and water added to make the volume 60 cc. A small funnel is placed in the neck of the flask to retard evaporation, and the solution boiled quietly for exactly half an hour. It is then cooled, nearly neutralized with sodium hydrate, and the dextrose determined by Fehling's solution. The method is simple and fairly accurate. A correction should be made for sugar in the malt extract. The malt extract is prepared by treating coarsely pulverized dry malt for several hours with sufficient 20 per cent. alcohol to cover it. The solution is then filtered, and may be kept for two weeks without losing its diastatic power.

# EXAMINATION OF FERMENTED LIQUORS.

## WINE.

Effervescing wines should, before analysis, be vigorously shaken in a large flask, to remove carbon dioxide.

*Specific Gravity.* — Specific gravity is taken by means of the pyknometer or Sprengel tube at 15.5° C.

*Alcohol by Weight.* — About 50 cc. of wine are weighed in a 150 cc. wide-mouth stoppered bottle, and transferred with 100 cc. water to a 500 cc. round bottom distilling flask. Free acid is neutralized with sodium hydrate, and 0.5 gram tannin added to prevent frothing. About 100 cc. of liquid are distilled over into the 150 cc. flask, which should be provided with a cork, perforated to receive the condenser-tip, and carrying a mercury valve to prevent loss of alcohol. The distillate, after being thoroughly mixed, is weighed, the specific gravity taken, and the percentage of absolute alcohol by weight corresponding to it found in the tables.

*Calculation of Results.* — Calling $A$ the percentage of absolute alcohol in the sample, $a$ that in the distillate, $W$ and $w$ their respective weights, then $A = \frac{wa}{W}$. If the specific gravity of the wine is known, weighing may be avoided by carefully measuring both sample and distillate at 15.5° C. The corresponding percentage of alcohol by volume may be found in the tables.

*Extract — Dry Wines.* — About 50 cc. are weighed in a small flask, transferred to a platinum dish having a flat bottom, and evaporated on the water bath to the consistency of sirup. The residue is then heated in the oven at 100° C. for two hours and a half, cooled in a desiccator, and weighed.

*Sweet Wines.* — Of these only 10 cc. are weighed, diluted to 100 cc., and 50 cc. evaporated as above described.

*Ash.* — Ash may be determined by igniting the extract at a very low red heat and weighing.

*Free Acids — Total Acidity Calculated as Tartaric Acid.* — 10 cc. of wine are titrated with $\frac{N}{10}$ sodium hydrate. The end-point is reached when a drop of the liquid placed upon faintly red litmus paper produces a blue spot in the middle of the portion moistened. Number of cc. $\frac{N}{10}$ sodium hydrate used $\times$ .0075 = weight in grams of all acids reckoned as tartaric acid.

*Volatile Acids Calculated as Acetic Acid.* — 50 cc. of wine are accurately measured into a 300 cc. flask provided with a cork having two perforations. One is fitted with a tube 6 mm. in diameter and blown out to a bulb 40 mm. in diameter a short distance above the cork; this tube is connected with a condenser. The other perforation carries a tube reaching nearly to the bottom of the flask and drawn out to a small aperture at its lower end; this is connected with a 500 cc. flask containing water. Both flasks are heated to boiling; the flame under that containing the wine is then lowered and the distillation continued by means of steam until 200 cc. have gone over. The distillate is titrated with $\frac{N}{10}$ sodium hydrate, using phenolphthalein as an indicator. Number of cc. $\frac{N}{10}$ sodium hydrate used $\times$ .0060 = weight in grams of volatile acids reckoned as acetic acid.

*Fixed Acids Calculated as Tartaric Acid.* — These may be found by calculating the volatile acids as tartaric and subtracting the result from the total tartaric acid found by direct titration.

EXAMPLE.

If 10 cc. wine by direct titration require 9.5 cc. $\frac{N}{10}$ alkali, 50 cc. require 47.5, therefore 47.5 $\times$ .0075 = .356 grams total acid reckoned as tartaric in 50 cc. If the distillate from 50 cc. wine requires 4.5 cc. $\frac{N}{10}$ alkali, then 4.5 $\times$ .0060 = .027 grams volatile acid reckoned as acetic. Now 4.5 $\times$ .0075 = .034 grams tartaric acid and .356 — .034 = .322 grams fixed acids reckoned as tartaric in the wine.

Results may be calculated in percentages or as grams in 100 cc. wine.

BEER AND OTHER MALT LIQUORS.

Before analysis the sample must be thoroughly shaken in a large flask, in order to remove carbon dioxide.

*Specific Gravity.* — Taken with the pyknometer or Sprengel tube at 15.5° C.

*Alcohol by Weight.* — Determined as in the analysis of wine, using 100 cc. of the sample.

*Extract and Ash.* — Determined as in the analysis of *dry* wines.

*Free Acids.* — Titrated as in the analysis of wine. Fixed acids, consisting principally of lactic and succinic, are calculated as lactic acid, using as a factor .0090. Volatile acids are calculated as acetic acid.

*Nitrogen.* — About 20 cc. of the sample are weighed, transferred to a digestion flask, and evaporated almost to dryness on the water bath. The nitrogen is then determined by Kjeldahl's method.

For the determination of other constituents of fermented liquors see authorities referred to below:

REFERENCES.

*U. S. Dept. Agric. Bull.* 43.
Allen, *Commercial Organic Anal. I.*
Sadtler, *Handb. Industrial Org. Chem.*
E. Borgman, *Anal. des Weines.*
Maercker, *Handb. der Spiritusfabrikation.*
Moritz and Morris, *Science of Brewing.*

# THE DETERMINATION OF CARBON DIOXIDE IN THE AIR OF BUILDINGS FOR THE PURPOSE OF ESTIMATING THE EFFICIENCY OF THE VENTILATION.

The determination is made by bringing a known volume of air in contact with some agent by which carbon dioxide is absorbed, forming a stable compound. The agents used are the hydrates of potassium, sodium, calcium, or barium. The first mentioned is used when it is possible to bring large quantities of air in contact with small quantities of solution; the potassium hydrate containing the carbonate may be kept for months (see "Transit of Venus Expedition," *Comptes rendus*, 1883, No. 21).

In the method as ordinarily carried out, calcium or barium hydrate is found the most convenient. The latter is preferred, since barium carbonate is less soluble and the reaction is sharper. In any case it is essential for the *complete* absorption of the carbon dioxide that the *reagent* should be largely in *excess*, so that no more than one fifth its value should be used up. The air of an ordinary laboratory contains 5 to 6 parts of $CO_2$ per 10,000. The exhaled breath contains, on an average, 400 parts, hence the necessity of caution in collecting samples and in handling the apparatus is evident.

## THE DETERMINATION.

### APPARATUS REQUIRED.

4 or 8 liter bottles graduated, with stoppers and caps; bellows and tube; 50 cc. bottles; pipettes; burettes; barometer and thermometer; hygrometer.

### CHEMICALS REQUIRED.

Barium hydrate 1 cc. = 1 milligram $CO_2$, approximately; sulphuric acid 1 cc. = 1 milligram $CO_2$ exactly; rosolic acid or phenolphthalein.

The bottles, previously clean and dry, are filled with the air to be tested by means of a bellows, a 6-foot rubber tube connecting them with a brass tube which reaches nearly to the bottom of the bottle; fifteen to twenty strokes will be sufficient to fill a 4-liter bottle. In collecting

the sample, care must be taken to avoid draughts or the proximity of people. It will be possible to obtain duplicate samples only in empty, or nearly empty, rooms. Even two sides of the room will probably show differences, but two bottles filled side by side ought to agree within 0.05 part per 10,000. The samples are brought into the laboratory, the temperature of which should be a trifle higher than that of the place where the samples were taken, and allowed to stand about half an hour, until they have attained its temperature. 50 cc. of the standard barium hydrate are now run in rapidly from a burette through the tube in the cork, the cap replaced, and the solution spread completely over the sides of the bottle while waiting three minutes for the draining of the burette. The bottle is now placed upon its side, and rolled or shaken at intervals for forty-five minutes; the time and the shaking are essential elements in the complete absorption, care being taken that the whole surface of the bottle is moistened with the solution each time. At the time at which the barium hydrate is added, the temperature and barometric pressure should be noted. At the end of the time the bottle is well shaken, to insure homogeneity of the solution, the cap is removed from the tube, and the large bottle is inverted over the 50 cc. glass-stoppered bottle, so that the solution shall come in contact with the air as little as possible. Under these conditions a full, well-stoppered bottle may safely stand for days before titration. An aliquot part, 25 cc., is taken for the titration, which should be made as rapidly as possible, a 100 cc. flask being used. The difference between the number of cubic centimeters of standard acid required to neutralize 50 cc. of barium hydrate before and after absorption gives the number of milligrams of dry carbonic acid in the sample tested. The amount of carbonic acid may be expressed in volumes, under standard conditions (0° and $760^{mm.}$), saturated with moisture (Method 1) or dry (Method 2). Tables for this purpose will be found in *Fres. Quan. Anal.*, § 139; *Ganot's Physics*, §§ 355–360; Bunsen, *Gasometrische Methoden*, p. 277; or Landolt and Börnstein's *Tables*.

## CALCULATION OF RESULTS.

*Method 1.* — 8.570 liters of air contained 10.8 mgs. of dry $CO_2$; 1 cc. $CO_2$ saturated with moisture at 21° and $766^{mm.}$ weighs 1.79624 mgs. (*Fres.*, § 139) ∴ 10.8 mgs. $= \frac{10.8}{1.79624} = 6.013$ cc. $CO_2$ saturated with moisture. In 10,000 cc. ∴ $\frac{6.013}{8570} = 7.02$ parts $CO_2$ per 10,000.

*Method 2.* $v^1 = v\,[(1 + .00366,\ t^1 - t)]$. $v^1 = 8570$ $\therefore$ $v = 7958$ cc. $t^1 = 21°$. $t° = 0°$. $v : v^2 :: H^2 : H$. $7958 : x :: 760 : (766 - 18.5)$ (18.5 = tension of aqueous vapor at 21°). $v^2 = 7827$ = capacity of bottle at 0° and $760^{mm.}$ 1 cc. $CO_2$ at 0° and $760^{mm.}$ weighs 1.9643 mgs. $\frac{10.8}{1.9643} = 5.50$ cc. $\frac{5.50}{7827} = 7.02$ parts $CO_2$ per 10,000.

NOTE. — *Two samples are to be taken following the notes closely, and the results calculated by both methods before collecting more samples.* Then some one room may be taken, and the quality of the air determined for the different hours of the day, or the same hour different days of the week, or a comparison of different rooms may be made, or a building may be tested as a whole. In making out the report of results they should be arranged in tabular form, attention being paid to the following points: Room, date, weather, barometer, time, place in room, number of people, or gas jets burning in room, and the condition of the doors, windows, and transoms.

REFERENCE.

*Jour. Analyt. and Applied Chem.* vol. vi., 363.

## BIBLIOGRAPHY OF THE CHEMISTRY OF FOODS.

A bibliography complete to 1882 may be found in the Second Annual Report of the New York State Board of Health. Some of the important works published since that time are given below:

Allen, "Commercial Org. Analysis," 2d ed.; Bell, "Analysis and Adulteration of Food;" Church, "Food" (South Kensington Science Handbook); Battershall, "Food and its Adulterations;" Atwater, "Chem. and Economy of Food" (U. S. Dept. Agric. Bull. 21, 1895); Richards, "Food Materials and Their Adulteration;" Atkinson, "Science of Nutrition;" Blyth, "Foods: Their Composition and Analysis;" Koenig, "Chemie der menschlichen Nahrungs-und Genussmittel," 3d auflage; Hilger, "Vereinbarungen bet. d. Unters. u. Beurteilung v. Nahr. u. Genussmittel;" "Bibliothek für Nahrungsmittel-Chemiker;" especially, Röttger, "Kurz. Lehrb. d. Nahrungsmittel-Chemie;" Ephraim, "Originalarbeiten über Anal. d. Nahrungsmittel;" Bujard and Baier, "Hilfsbuch für Nahr. Chemiker;" U. S. Dept. Agric. Bulletins 13, 43; Boards of Health Reports; Sadtler, "Indust. Org. Chem.;" Wiley, "Agricultural Analyses;" Addyman, "Agricultural Analysis." *Periodicals*—"Arbeiten aus d. Kaiserl. Gesundheitsamte zu Berlin;" "Analyst;" "Jour. Soc. Chem. Indust.;" "Vierteljahrsschrift für Chem. d. Nahr. u. Genussmittel;" "Milch Zeitung;" "Deutsche Viertelj. für öff offentl. Gesundheitspflege;" "Rapports du Laboratoire Municipal Paris."

# LABORATORY NOTES ON WATER ANALYSIS.

(Prepared for the use of students in the Laboratory of Sanitary Chemistry of the Massachusetts Institute of Technology. Not published.)

## CLASSIFICATION OF WATERS.

THE examination of a water in order to determine its fitness for domestic use (a so-called sanitary analysis) comprises the determination of three points: first, the amount, if any, of organic matter in a living or dead condition suspended or dissolved in the water; second, the amount and character of the products of decomposition of organic matter, and their relative proportions to each other; and third, the amount of certain mineral substances dissolved in the water. From these results we draw conclusions as to the present condition and past history of the water.

To facilitate this examination waters may be divided into three classes: first, brook, pond, and river water — so-called surface water; second, spring and deep well water; third, shallow wells and sewage effluents.

The waters of the first class found in New England are generally more or less colored, and contain more or less suspended organic life and its *débris*, which often impart a decided odor to the water. These waters, draining for the most part wooded and sparsely populated regions, are low in ammonia, nitrites, and nitrates; low, also, in mineral salts, and with only a slight excess of chlorine over the normal. They are usually high in organic matter and albuminoid ammonia.

The waters of the second class are generally odorless, colorless, without suspended matter or organic matter in solution, low in nitrates, and with nearly normal chlorine, but with higher mineral substances than surface waters.

Waters of the third class present the greatest variety. They may be as clear and colorless and as free from organic matter as the second class, and they may contain more organic matter than some waters of the first class. As a rule, nitrates and chlorides, as well as mineral salts, are high; ammonia and nitrites may or may not be high.

It is always desirable to know something about the origin and character of a water before beginning the analysis, and the foregoing general classification will be found helpful in planning the analysis. In addition to classifying a water in this way it will also be found useful to make three qualitative tests: first, with Nessler reagent to see if much free ammonia is present; second, with silver nitrate for the amount of chlorine; and third, with phenol-disulphonic acid for nitrates.

Since the condition of the organic matter and the relation of the several products of decomposition to each other are constantly changing, the determination of these should be begun without delay. The determination of the so-called "free ammonia" is first made after distilling the apparatus free from ammonia. Then follows the distillation with alkaline permanganate in order to liberate the nitrogen in the undecomposed organic matter; this product is called "albuminoid ammonia." The determination of the total combined nitrogen by the Kjeldahl process is to be carried on in waters of Class I at the same time if practicable.

The test for the amount of nitrogen in the second product of decay, nitrites, is also made as soon as possible, and lastly the required quantity of the sample is set aside to be evaporated for the determination of nitrates.

The odor of the water is at times a valuable aid in judging the condition of a surface or well water. This should be determined on the first day and while the bottle is at least half full. It often happens that the color of the water gives also valuable information as to its condition.

The examination for turbidity and sediment is made on the morning of the second day after the bottle has stood over night. The color is estimated at any convenient time during the two days. The determination of the carbon in the organic matter, which is in such a condition as to be oxidized to $CO_2$ by the Kubel method by treatment with hot, acid, potassium permanganate solution, is next in order, and the results are expressed as "oxygen consumed."

The final test for the presence of organic matter in waters of Class I is made by igniting the total solid residue on evaporation.

This determination has little or no value in the case of Classes II and III, and is omitted as a rule.

The residue on evaporation is often used for the determination of iron.

The determination of chlorine is most essential in deciding upon the history of a water, since chlorine is not taken up by plant life as nitrogen is, and, being soluble in all combinations, it remains in the water when once it is there.

Hardness is determined by means of a soap solution, and expresses approximately the amount of calcium and magnesium salts present. The determinations of the fixed solids, hardness, chlorine, nitrates, and iron, taken together, give a good idea of the character of the mineral matters dissolved in the water.

Having obtained these several results, there remains the decision as to the present condition and past history of the water as shown by these tests. Briefly, the questions to be answered are these:

I. Is the water a normal unpolluted water of its class? that is, has it any more of any substance than it has a right to contain by virtue of its source? A brook draining a meadow or swamp has color, gives high albuminoid ammonia and high oxygen consumed, but it is not on that account a "polluted" water. A well water may contain high nitrates and chlorine and yet be free from present pollution. A deep well water may contain high free ammonia without giving any evidence of pollution in historic time. To answer the question, therefore, one should know the locality and surroundings of the water, its source, the normal chlorine, the ratio of the nitrogen compounds to each other, and its character as regards the permanence of the organic matter it contains.

II. Is the water, if normal, a good water for general domestic uses? that is, is it hard or soft, has it much or little iron, has it any disagreeable odor?

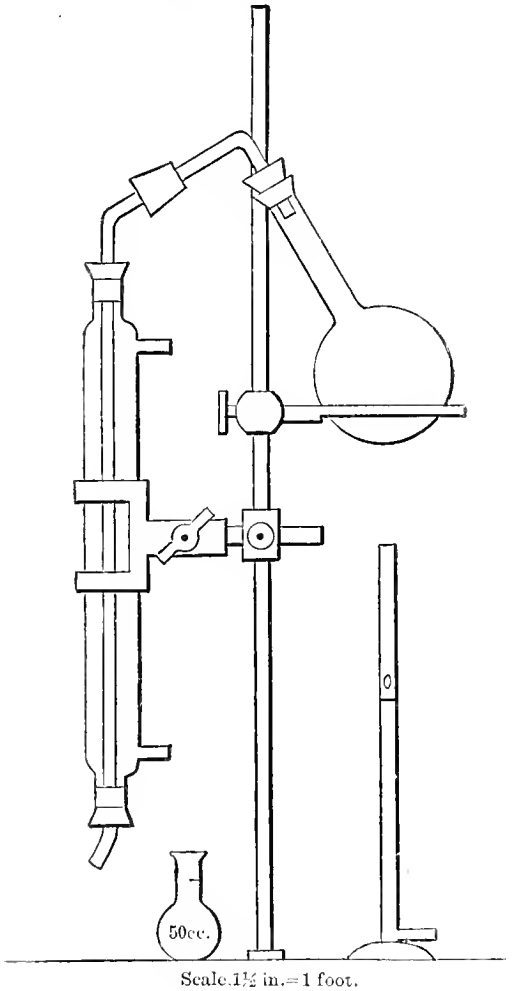
III. Is the water in any case safe for drinking? To answer this question there is needed a knowledge wider than a chemist's of the relation of decaying organic matter and of the germ-carrying power of water to outbreaks of disease. To the chemist's knowledge must be added, therefore, that of the biologist, the engineer, and the sanitarian.

# METHODS AND REACTIONS.

## FREE AND ALBUMINOID AMMONIA.

Since the condition of the nitrogen, as well as the relative proportion of each of the four forms in which it occurs, is one of the most important points to be decided, the determination of the first product of decay, the so-called free ammonia, is begun at once. The test is one of much delicacy, and requires the greatest care and cleanliness of manipulation. The top of the bottle is first rinsed under running water to free it from any possible dust. Under no circumstances must the inside of the neck of the bottle or the stem of the stopper be touched by the hand or wiped with a cloth.

After the contents of the bottle are well shaken, in order that an average sample may be obtained, a measured portion is distilled in the apparatus shown in the accompanying cut, after it has been freed from all traces of ammonia by distilling in it ammonia-free water.



Scale 1½ in. = 1 foot.

Of Classes I and II 500 cc. are usually taken; of Class III 500 or less — sometimes only 10 cc. are used, according to the result of the qualitative test. To this latter class of waters about 0.5 gram of sodium carbonate is added to be sure that the reaction is not acid. Three portions of the distillate, of 50 cc. each, are caught in graduated flasks and set aside. If there is very much free ammonia present 200 cc. are distilled over. The time of distilling 50 cc. should not be more than eight or less than five minutes.

After the free ammonia has been distilled off and the contents of the flask have slightly cooled, 40 cc. of alkaline permanganate are added through a funnel, taking care that no alkali touches the neck of the flask, and the distillation of

the albuminoid ammonia, that is to say, the determination of the nitrogen of the undecomposed organic matter, is proceeded with. For Class I five portions of 50 cc. each are obtained; for Classes II and III only four portions are taken. This process gives about one half of the total combined nitrogen in the waters of Class I.

The contents of the 50 cc. receiving flasks are transferred to Nessler tubes to be compared with standards which are prepared as follows: To the Nessler tubes nearly filled with water free from ammonia is added varying quantities, for instance, 0.3, 0.5, 0.7, 1.0, 1.3, 1.5, 2.0, 2.5, 4.0, 6.0 cc. of a standard solution of $NH_4Cl$ containing .00001 gram $NH_3$ in 1 cc.

The contents of the tubes are rotated (never shaken like test tubes or stirred with a rod), allowed to stand two or three minutes, and 2cc. of the Nessler reagent added to the whole set and to the samples to be tested as rapidly as possible. At the end of ten minutes the colors are matched and the amount of ammonia recorded. As an example of a water of Class I may be given the following results from distilling 500 cc.:

| FREE AMMONIA. | | ALBUMINOID AMMONIA. | |
|---|---|---|---|
| 1st 50 cc. | 0.7 cc. | 1st 50 cc. | 4.5 cc. |
| 2d 50 cc. | 0.3 cc. | 2d 50 cc. | 2.8 cc. |
| 3d 50 cc. | 0.0 cc. | 3d 50 cc. | 1.5 cc. |
| | | 4th 50 cc. | 1.0 cc. |
| | | 5th 50 cc. | 0.5 cc. |

In this case the free ammonia would be .0020, and the albuminoid ammonia .0206 parts per 100,000.

The compounds produced by action of ammonia on mercuric solutions are considered as substitutions of 1Hg for 2H in $NH_4$ and are called mercur-ammoniums. Tetra-mercur-ammonium iodide ($NHg_2I$) is a brown precipitate soluble in excess of KI in presence of KOH with a brown yellow color, proportionate to the amount of $NH_3$.

$$NH_3 + (2HgI_2 + 2KI + 3KOH) = NHg_2I + 5KI + 3H_2O.$$

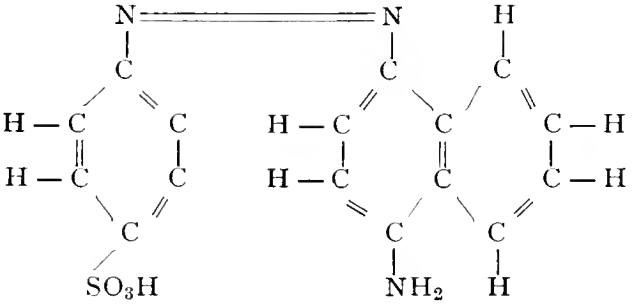
If practicable, a determination of the total nitrogen in the organic matter should be carried on at the same time by the Kjeldahl process. (See page 7.)

NITRITES.

As soon as the foregoing determinations are well started the test for the second product of decay, the nitrites, is made. Waters of Class I must be freed from color by milk of alumina, and filtered through

filters washed with nitrite-free water. 100 cc. of the colorless water are treated in special tubes with three reagents, added in the following order and quantities: 1 cc. HCl 1 : 4, 2 cc. sulphanilic acid, 2 cc. naphthylamine hydrochlorate. The filtration and determination should be carried on within the half hour, since the air of any room in which gas is burned contains nitrites.

The pink color of the azo *a* amidonaphthylic parabenzolsulphonic acid,



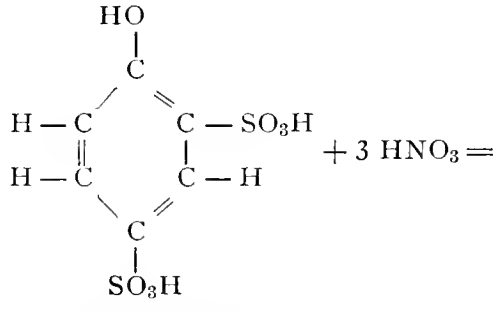
which is formed when nitrites are present, is compared with that of known amounts of standard nitrite solution, containing .0000001 gram N in 1 cc. Sewage effluents and waters from bad wells often need to be diluted, 10 cc., or even 1 cc., being made up to 100 cc. before adding the reagents.

### NITRATES.

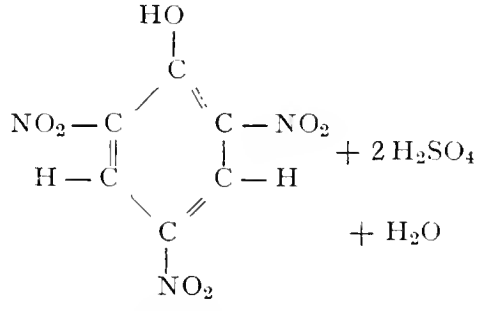
Nitrogen in the third stage, that of nitrates, is next determined. In case of colorless well waters, 1 cc. and 2 cc. are measured out with a capillary pipette into $2\frac{1}{2}$-inch porcelain dishes and set away to evaporate spontaneously in a place free from dust. For surface waters, always low in nitrates, 10 cc. are taken from the decolorized portion filtered for nitrites, and the dishes are placed on the top of the water bath until the bulk is reduced to about 2 cc., when they are set away to evaporate spontaneously.

This determination depends on the color given by an ammoniacal solution of trinitrophenol (picric acid), which in this case is formed by the action of the nitrates contained in the cold, dry residue upon the phenol-disulphonic acid with which it is moistened. Six or eight drops of the acid are run directly upon the residue and carefully rubbed into it with a short glass rod to insure complete contact of the acid and the residue in the dish. After a moment or two 7 cc. of water are added, and 3 cc. of an alkali (preferably ammonia), to distinct alkaline reaction.

The yellow color thus produced is compared with standards, 1 cc. .000001 gram N, in the same way as in the two previous tests.[1]




phenol-disulphonic acid.




picric acid.

KJELDAHL PROCESS FOR TOTAL ORGANIC NITROGEN.

Five hundred cc. of the water are poured into a round-bottomed flask, of about 900 cc. capacity, and boiled until 200 cc. have been distilled off. The free ammonia which is thus expelled may, if desired, be determined by connecting the flask with a condenser. To the water remaining in the flask is added, after cooling, 10 cc. of pure concentrated sulphuric acid. After mixing, the flask is placed in an inclined position on wire gauze, on a ring-stand or other convenient support, and boiled cautiously, until all the water is driven off and the concentrated sulphuric acid is white or a very pale yellow. After cooling, 200 cc. of water free from ammonia are added, the neck of the flask being washed free from acid, and then 100 cc. of sodium hydrate solution. The flask is immediately connected with the condenser and then shaken to mix the contents.

The distillation at the start is conducted rather slowly. After the first 50 cc. are condensed, the contents of the flask may be boiled more rapidly until 150 cc. to 175 cc. have altogether been collected. The total distillate is made up to 250 cc. with water free from ammonia, well mixed, and 50 cc. taken for nesslerization.

The sulphuric acid oxidizes the carbon of the organic matter, thus liberating the nitrogen in the form of $NH_3$ which remains as $(NH_4)_2SO_4$ until released by distillation with NaOH.

The Kjeldahl process is very much simpler as applied to waters than it is for many organic substances — flour, for instance. The organic

[1] References: Sprengel, Pogg. Ann. 121, p. 188; Grandval and Lajoux, Compt. Rend. 101, p. 62; Fox, Tech. Quar. 1, p. 1; Hazen & Clark, Jour. Anal. & App. Chem. 5, p. 1, Gill, Jour. Am. Chem. Soc. 16, 122.

matter in surface waters can be easily oxidized by sulphuric acid without the aid of potassium permanganate or mercury.

### CARBONACEOUS MATTER, OR "OXYGEN CONSUMED."

*Kubel's Hot Acid Method.*

100 cc. (or 25 cc. of very highly colored waters) are measured into a 250 cc. flask. 8 cc. of $H_2SO_4$ (1 : 3), and 10 to 20 cc. of standardized, approximately $\frac{N}{100}$ permanganate added, the whole boiled for five minutes and cooled one minute. The color is then discharged by 10 cc. of exactly $\frac{N}{100}$ oxalic acid and the solution titrated with the permanganate to a faint permanent pink. Since 1 cc. of the oxalic acid corresponds to .00008 gram oxygen, the number of cubic centimeters of permanganate which have been used to oxidize the organic matter must be multiplied by its value referred to the oxalic acid as a standard.

Example. 11 cc. permanganate solution are decolorized by 10 cc. oxalic acid; 1 cc. of permanganate has, therefore, a value of .000072 gram oxygen.

100 cc. of the sample of water + 10 cc. oxalic acid required 14 cc. permanganate.

14 cc. — 11 cc. = 3 cc. × .000072 = .000216 oxygen; or expressed in parts per 100,000 — .2160.

### CHLORINE.

Colored surface waters are treated with milk of alumina to remove the color as follows: About 750 cc. are poured, without measuring, into a flask holding at least one liter, 3 to 5 cc. of the alumina added, and the water brought to the boiling point. The flask is now set aside in an inclined position so that the alumina may settle out and allow of the decantation of two measured portions of 250 cc. each, which are concentrated in six-inch evaporating dishes on the steam bath to 25 cc. A clean feather, moistened with distilled water, is used to rub the sides of the dish and loosen any adhering residue. Three drops of a neutral solution of potassium chromate are added, and the solution titrated (in the same evaporating dish in which it was evaporated) with silver nitrate, with or without the addition of sodium chloride. The latter solution has always a strength of 0.001 gram Cl in 1 cc. The silver nitrate is usually one half the value. Colorless waters of Classes II and III do not need to be treated with milk of alumina. If high in chlorine, 25 cc. may be titrated directly; if low in chlorine, 250 cc. are concentrated as above.

### RESIDUE ON EVAPORATION.

A portion of the water to be examined (200 cc. of waters of Class I, 100 cc. of waters of Classes II and III) is evaporated in a weighed platinum dish on a water bath. After drying in an oven at 100°C. for two or three hours, the dish is left in the desiccator over sulphuric acid for some hours.

This gives the total weight of inorganic matter contained in the water, and in case of the waters of Class I of the organic matter as well. This latter may be burned off in the radiator, leaving "fixed solids" or mineral matter.

### HARDNESS.

The amount of soap solution required to give a foam or lather with 50 cc. of water, which remains five minutes after shaking in a 250 cc. bottle, is read from the burette, and the corresponding quantity of calcium carbonate (or other salts) is taken from the table given in *Sutton's Volumetric Analysis*, page 370.

### DISSOLVED OXYGEN.

#### *Winkler's*[1] *Method.*

When water is taken from a faucet, a glass-stoppered bottle of known capacity, holding from 50 to 250 cubic centimeters, is filled by means of a tube which passes to the bottom of the bottle. A considerable amount of water is allowed to pass through the bottle and overflow at the top. In taking samples from streams or ponds a stopper with two holes is used. A tube passing through one of these holes is sunk in the water to the desired depth, and the other is connected with a larger bottle of at least four times the capacity of the smaller one and fitted in the same way. From the larger bottle the air is exhausted by the lungs or by an air pump until it is nearly filled with water. Unless the determination is to be made at once the rubber stopper in the smaller bottle is quickly replaced by the glass stopper, so that no air is left in the bottle.

In making the determinations a small amount of a saturated solution of manganous sulphate is added with a pipette having a long capillary point reaching below the surface of the water, and in the same way a concentrated solution of potassium iodide and sodium hydrate. The glass stopper is now inserted, leaving no bubble of

[1] Berichte der deutsch. chem. Gesell., Vol. XXI, p. 2843.

air, and the contents well mixed. Strong hydrochloric acid is added, after most of the precipitate has settled to the bottom of the bottle. The contents of the bottle are now poured into a flask or other convenient vessel, and the liberated iodine (in amount proportional to the amount of dissolved oxygen in the water) is titrated with thiosulphate.

In calculating the amount of oxygen, a correction must be made for the volume of the reagents used, which should not be more than 1 per cent of the total volume. If the precipitate had settled before the acid was added no allowance should be made for the amount of acid, since the water it displaces contains no oxygen or iodine. If water is collected in the ordinary way and transferred to the apparatus by pouring, there will inevitably be an absorption of oxygen, unless the water is already saturated. Thus a process which gives excellent results when the water is nearly or quite saturated may fail entirely to give accurate results when the dissolved oxygen is low or absent.

The results are reported in "percentage of saturation," the amount of oxygen which water will take up at the observed temperature being used as a basis. Winkler has calculated these amounts from 0° to 30°.[1] It frequently happens that percentages greater than one hundred are obtained, due to the supersaturation of the water with oxygen.[2]

Determinations of dissolved oxygen in ponds and streams are best made on the spot. The very simple apparatus required for the Winkler process can be packed in small space, and the entire determination requires only a few minutes. The absorption of the oxygen by the manganous hydrate is complete almost at once, and it is unnecessary to allow it to settle for a long time before adding acid. The titration can be made with a small burette or pipette with accurate results.

The temperature of the water at the depth from which the sample is taken is conveniently determined by means of a thermometer fitted by a doubly-perforated stopper to a bottle of about 500 cc. capacity, which has been filled with some of the water and then lowered to the desired depth.

## IRON.

Treat the residue on evaporation of 200 cc. of water with about 5 cc. of HCl (strong acid diluted with an equal bulk of water) on a water bath, being careful to carry the acid nearly to the edge of the dish to insure its contact with all the residue. When the residue is

[1] Berichte, Vol. XXII, p. 1772.

[2] Technology Quarterly, Vol. V, p. 250.

completely dissolved (with the exception of silica), the solution is rinsed with a 100 cc. tube and diluted to about 50 cc. A solution of permanganate is added drop by drop until the liquid remains pink for at least ten minutes.

After the pink color has faded 15 cc. of a solution of potassium sulphocyanate (5 grams to the liter) is added, and after twenty minutes the color is read, using standards made up at the same time from a solution of which 1 cc. contains 0.0001 gram of iron.

The greatest care is necessary to prevent access of dust and to exclude any possible contamination; also to avoid loss of ferric chloride by overheating, and in ignited residues to secure the complete solution of the iron.

The results, with due precaution, have been very satisfactory.[1]

## ODOR.

The odor of waters is obtained by shaking violently the sample in one of the large collecting bottles when it is about one half full, then removing the stopper and quickly putting the nose to the mouth of the bottle. An odor can often be detected in this way which would be entirely inappreciable if the water were poured into a tumbler. The odor which is given off when a water is heated is sometimes the same as the odor of the water when cold, sometimes it is different. The hot odor is obtained by heating on an iron plate about 200 cc. of the water in a beaker of 500 cc. capacity covered with a watch glass. The water is quickly heated until the air bubbles have all been driven off and the water is about to boil. The beaker is then taken off the plate, and, after cooling for about five minutes, it is shaken by a rotary movement, the watch glass removed, and the nose put inside the beaker. It is only for an instant, as a rule, that an odor can be perceived.

## COLOR.

Most of the surface waters of the State have a yellowish-brown color more or less pronounced. The tint corresponds, particularly in the lower grades, very closely to that of nesslerized ammonia, so that the standards for reading ammonia can be used also for the determination of the color. The comparison is made in the same kind of 50 cc. tubes that are used for the ammonia determinations, but the tubes used for this purpose are kept separate from those used for the ammonia, since the least amount of alkali remaining in a tube (if im-

[1] Thomson, Journ. Chem. Soc., Vol. XLVII, p. 493, 1885.

perfectly washed) alters the color of the water. The scale used corresponds with the amount in the standards. Thus a color of 1.0 is that corresponding to the nesslerization of 1 cc. of the standard ammonium chloride solution ; 0.1 is the color produced with 0.1 cc. of this solution. In the higher grades of color, over 1. the tint varies considerably from the nesslerized ammonia, and the degree of color is then better determined in wider tubes and in less depth. Standards made from very dark water from cedar swamps by various degrees of dilution, and verified by direct comparison with nesslerized ammonia, are also used.

### TURBIDITY AND SEDIMENT.

The suspended matter remaining in the water after it has rested quietly in the collecting bottle for twelve hours or more is called its turbidity, and that which has settled to the bottom of the bottle its sediment.

Good ground waters are often entirely free from turbidity and sediment, but surface waters are seldom free from suspended matter. The turbidity is very various in character and amount, sometimes milky from clay, but more generally it consists of fine pollen-like particles. These are generally living algæ or infusoria, and a practiced eye can, not infrequently, recognize their forms. Some of the lower animal forms can also be seen by the naked eye, and the larger Entomostraca are quite noticeable in many waters.

The sediment may be earthy or flocculent, in the latter case it is generally *débris* of organic matter of various kinds. The degree of turbidity is expressed by the terms "very slight," "slight," "distinct," and "decided," and the degree of sediment by "very slight," "slight," "considerable," and "heavy."

## REAGENTS.

*Nessler Reagent.* — Dissolve 61.750 grams KI in 250 cc. distilled water. Add 415 cc. of a cold solution of $HgCl_2$ which has been saturated by boiling an excess of the salt and allowing it to crystallize out. Dissolve the slight precipitate of $HgI_2$ by adding 0.750 gram powdered KI. Then add 300 grams of KOH dissolved in 250 cc. of water. Make up to the liter and allow it to stand over night to settle. This solution should give the required color with ammonia within five minutes, and should not precipitate within two hours.

*Alkaline Permanganate.* — Dissolve 400 grams of refined potassium carbonate in 2 liters of distilled water and heat to boiling in a silver

dish. After removing the lamp add 250 grams of quicklime of the best quality piece by piece. When all the lime is slaked, heat to boiling again, and transfer to a large bottle or crock which can be tightly closed to exclude the air. Allow it to settle over night, siphon off the clear liquid, and add water until the sp. gr. = 1.125. One liter of this caustic potash and 8 grams of permanganate crystals are boiled for thirty minutes, the water lost on evaporation being replaced. When the chemicals used are all good there should be no correction needed for ammonia in this solution.

*Standard Nitrite Solution.* — The pure silver nitrite used in making this solution is prepared by the double decomposition of silver nitrate and potassium nitrite and repeated crystallizations from water of the rather insoluble silver nitrite. 1.1 grams of this silver nitrite are dissolved in water nitrite-free, the silver completely precipitated by the addition of the standard salt solution used in the determination of chlorine, and the solution made up to one liter. 100 cc. of this strong solution are diluted to 1 liter, and 10 cc. of this last solution again diluted to 1 liter. The final solution is the one used in preparing standards. 1 cc. = .0000001 gram of nitrogen.

*Sulphanilic Acid.* — Dissolve 8 grams (Kahlbaum's) in 1 liter of water. This is a saturated solution.

*Naphthylamine Hydrochlorate.* — Dissolve 8 grams in 992 cc. of water and add 8 cc. strong HCl. (Keep in the dark.)

*Standard Nitrate Solution.* — 0.720 gram of pure $KNO_3$ is dissolved in 1 liter of water. Of this strong solution 10 cc. are diluted to 1 liter. 1 cc. of this dilute solution corresponds to .000001 gram nitrogen.

*Phenol-Disulphonic Acid.* — Heat together 3 grams synthetic phenol with 37 grams pure concentrated $H_2SO_4$ on a boiling water bath for six hours.

*Sodium Hydrate.* — For Kjeldahl process. Dissolve 200 grams good quality caustic soda in 1 liter of water. Boil with 3 grams of permanganate crystals to free the solution from nitrogen.

*Sulphuric Acid.* — For Kjeldahl process. This should be free from nitrogen. May be obtained from Baker & Adamson, Easton, Penn.

*Calcium Chloride and Soap Solutions.* — For hardness. Dissolve 0.200 gram of pure Iceland spar in dilute HCl, and evaporate several times to remove excess of acid. Dissolve the calcium chloride thus formed in 1 liter of water. Dissolve 100 grams best dry white Castile soap in 80 per cent alcohol. From this strong solution make a weaker solution (about 100 cc. to a liter of 70 per cent alcohol) of such a

strength that 14.25 cc. will give the required lather with 50 cc. of the above $CaCl_2$ solution.

*Reagents for Winkler's Process.* — 360 grams of NaOH and 100 grams of KI in 1 liter of water.

48 grams of $MnSO_4 + 4H_2O$ in 1 liter of water. HCl sp. gr. 1.125.

Thiosulphate $\frac{n}{10}$ + 4 grams ammonia carbonate. Dilute to $\frac{n}{100}$ for use. Standardize by potassium bichromate.

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The following books will be found on the laboratory shelves for consultation as to methods of analysis and interpretation of the results obtained:

Wanklyn — Water Analysis.
Frankland — Water Analysis.
Nichols — Water Supply.
State Board of Health Reports for Massachusetts.
" " " " " " Michigan.
" " " " " " Illinois.
National Board of Health Report for 1882.
Tiemann-Gærtner — Untersuchung des Wassers.
Fischer — Die Chemische Technologie des Wassers.

The following papers on special topics relating to water supply and water analysis will be found in the reports of the Massachusetts State Board of Health, the Proceedings of the Society of Arts, and the Technology Quarterly. They are also available in pamphlet form:

The Chemical Examination of Water.
The Interpretation of Water Analyses.
Chemical Examination of Drinking Water.
Discussion of Special Topics relating to the Quality of Public Water Supplies.
The Analysis of Water — Chemical, Microscopical, and Bacteriological.
On the Determination of the Organic Nitrogen in Natural Waters by the Kjeldahl Method.
On the Amount of Dissolved Oxygen contained in Waters of Ponds and Reservoirs at Different Depths.
On the Amount of Dissolved Oxygen contained in the Waters of Ponds and Reservoirs at Different Depths in Winter, under the Ice.
The Odor and Color of Surface Waters.
The Effect of the Aeration of Natural Waters.
The Filtration of Natural Waters.
On the Mineral Contents of Some Natural Waters in Massachusetts.
The Purification of Water by Freezing.

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